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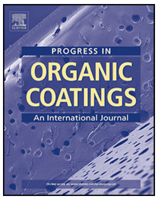

Synthesis, characterization and evaluation of urethane co-oligomers containing pendant fluoroalkyl ether groups

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ABSTRACT

Coatings with the ability to minimize adhesion of insect residue and other debris are of great interest for future aircraft. These aircraft will exhibit increased fuel efficiency by maintaining natural laminar flow over greater wing chord distances. Successful coatings will mitigate the adhesion of debris on laminar flow surfaces that could cause a premature transition to turbulent flow. The use of surface modifying agents (SMA) that thermodynamically orient towards the air side of a coating can provide specific surface chemistry that may lead to a reduction of contaminate adhesion. Aluminum surfaces coated with urethane co-oligomers containing various amounts of pendant fluoroalkyl ether groups were prepared, characterized and tested for their abhesive properties. The coated surfaces were subjected to controlled impacts with wingless fruit flies (*drosophila melanogaster*) using both a benchtop wind tunnel and a larger-scale wind tunnel test facility. Insect impacts were recorded and analyzed using high-speed digital photography and the remaining residues characterized using optical surface profilometry and compared to that of an aluminum control. It was determined that using fluorinated oligomers to chemically modify coating surfaces altered the adhesion properties relative to the adhesion of insect residues to the surface.

1. Introduction

As part of an effort to develop coatings to minimize the adhesion of undesirable substances to aerospace surfaces, research has been conducted on the synthesis, characterization and evaluation of urethane based coatings containing surface modifying agents (SMAs). NASA has several on-going and planned future projects with a need for surface engineered materials that mitigate or minimize the adhesion of a variety of species in diverse, and extreme environments. For example, preventing dust particles that might be encountered in extraterrestrial environments from accumulating on a solar array [1], ice and water droplets from accumulating during aircraft flight [2], or preventing insect residue from adhering to future aircraft surfaces thereby disrupting laminar flow, increasing drag and reducing fuel efficiency [3]. Laminar flow wings and airflow surfaces are envisioned as advantageous design features for future aircraft because of the reduced drag and resultant improvement in fuel efficiency. However, it is known that laminar flow can be perturbed by imperfections on the airflow surface. The size, particularly height, and location of the imperfection are important, but the exact dimensional features are highly dependent on the flight conditions, and are thus hard to pinpoint with precision. However, studies are underway within NASA to assess these issues. Insect residue is the primary candidate that can adhere to airflow surfaces and potentially cause disruption in the airflow over laminar surfaces and cause a concomitant increase in drag. This is a performance issue not a safety concern. A number of effective techniques to modify the surface chemistry of polymeric materials have been investigated including chemical or physical vapor deposition [4], self-assembled monolayers [5], surface-confined chemical reactions [6], block co-polymers [7], SMAs [8] and polymer brush growth [9,10]. The approach described herein uses SMAs in the form of commercially available hydroxyl terminated oxetane-derived oligomers containing pendant fluoroalkyl groups that are co-reacted with toluene diisocyanate and 1,4-butanediol to form controlled molecular weight random co-oligomers.

SMAs are thermodynamically drawn to the air side surface of a material enabling controlled surface chemical modification with minimal SMA incorporation [9,11]. This alters the surface energy which can dramatically affect properties such as wettability and adhesion, however the bulk properties of the base polymer are largely unchanged because effective SMA loading levels are

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typically less than 1% (w/w) [12]. Fluorine and silicon containing species are well known to migrate to the air side of polymeric based coatings [13]. In fact, in many applications where adhesive bonding is important, great lengths are often employed to avoid contamination by silicon and fluorine containing species due to their known difficulty in forming adhesive bonds. Of the two, fluorine containing species have a greater proclivity for surface migration than silicon containing species and have been demonstrated to undergo surface migration when incorporated into a variety of polymer types including polyesters [14], polyurethanes, polyacrylates, polydimethylsiloxane and polyimides [15].

Polyurethanes have an excellent combination of physical and mechanical properties that make them useful in a broad array of applications [16]. A number of studies involving structure property relationships of polyurethanes have been reported and the topic reviewed [17]. Fluorine containing diols have been used in polyurethane synthesis to create polymeric films with low surface energy. For example, Tang et al. [18] reported polyurethanes modified with 5% of a fluorinated diol that exhibited water surface wetting characteristics comparable to that of a fully fluorinated polymer, e.g. Teflon®, with no measureable loss of bulk properties. However, a complete understanding and concomitant ability to prevent adhesion of complex, active and dynamic chemical systems such as those encountered with biological species remains a significant challenge. The modification of surface energy alone has proven to be insufficient to prevent such materials from adhering to polymeric surfaces. Other approaches have used SMAs to ferry other chemically active species to a material surface which otherwise would not spontaneously surface migrate [19].

In this work, the synthesis of controlled molecular weight urethane co-oligomers with various amounts of fluorinated oligomeric diols is presented. The materials were characterized for surface properties, spray coated onto aluminum substrates, and tested for their ability to prevent insect residue from adhering to the coating surface in a benchtop wind tunnel and a larger-scale wind tunnel test facility.

2. Experimental

2.1. Materials and methods

Hydroxyl-terminated PolyFox-656 (PF-656) was purchased from Omnova Solutions and used as received. 1,4-Butanediol (BD) was obtained from Sigma Aldrich and dried for 72 h over 3 Å molecular sieves prior to use. 2,4-Toluene diisocyanate (TDI) from Sigma Aldrich was used as received. The catalyst, dibutyltin dilaurate, was used as received from Sigma Aldrich. Anhydrous dimethylformamide (DMF) was purchased from Sigma Aldrich and stored over 3 Å molecular sieves and filtered using a fritted glass funnel prior to use. Methyl ethyl ketone (MEK) was used as received. ^{1}H NMR spectra were recorded on a Bruker (Avance 300) multinuclear spectrometer operating at 300.152 MHz. Spectra were collected in either $CDCl_3$ or d_6-DMSO. Polymer films were spray coated from 8% w/w solutions in MEK onto aluminum panels [Al 1100, 3 mil (76.2 μm) thickness] and dried in a low humidity chamber under flowing air. Prior to coating, the Al panels were wiped with isopropanol. Energy-dispersive X-ray spectroscopy (EDS) studies were conducted using a Thermo Scientific Noran System 7 X-Ray microanalysis system attached to a Hitachi S-5200 field emission scanning electron microscope (SEM). Samples were sputter-coated with a thin layer (∼3 nm) of Au/Pd prior to analysis. The acceleration voltage during the analysis was 10 kV. EDS spectral acquisition and mapping were both conducted at Rate 5 and 7 as set by the instrument software, which has a maximal throughput of 227,000 cps and 417,600 cps, respectively, for 30 frames at 10 s/f.

Table 1
Percentage of hard segment and soft segment content in urethanes.

Oligomer	Mole percent Hard segment	Mole percent Soft segment
Urethane 0	100	0
Urethane 1	99	1
Urethane 5	95	5
Urethane 10	90	10
Urethane 20	80	20
Urethane 30	70	30
Urethane 100	0	100

2.2. Urethane co-oligomer synthesis

Using the general procedure outlined in this section, controlled molecular weight (5000 g/mol) random urethane co-oligomers were prepared by reacting 2,4-toluene diisocyanate (TDI) with various combinations of the BD and PF-656 (Table 1). The diol content in the NCO/OH molar ratio was always in excess to control the molecular weight (∼5000 g/mole) and to minimize the presence of reactive isocyanate end groups. In a flame dried 3-necked round bottomed flask equipped with a mechanical stirrer, the diols were added along with DMF. Dibutyltin dilaurate catalyst (1 wt%) was added to the flask and the solution was stirred and heated to 75 °C. Upon heating, the diols dissolved in the DMF to form a light yellow solution. TDI was added drop-wise over ∼20 min while maintaining the temperature around 75 °C. The reactions were carried out at 20 wt% solids under a nitrogen atmosphere over about a 16 h period, resulting in a colorless solution with a moderate increase in solution viscosity. The reaction was then cooled to room temperature and precipitated in deionized water with vigorous stirring, filtered using a fritted glass funnel, washed multiple times in water and dried under vacuum at 80 °C overnight. The white powders were obtained in near quantitative yields. The urethane co-oligomer was characterized by DSC, FTIR, and ^{1}H NMR.

2.3. Differential scanning calorimetry

Differential scanning calorimetry (DSC) data were obtained from a Setaram 131 system under a nitrogen atmosphere at a scan rate of 20 °C/min. A standard heat/cool/heat profile was used in running the samples. Heating the urethanes above their transition temperatures and cooling at a controlled rate erased the previous thermal history of the urethanes. The second heat cycle was used to evaluate the intrinsic properties of the urethanes [20]. The samples were initially heated to 200 °C and then cooled from 200° to −30 °C and heated at 20 °C/min to 200 °C. Glass transition data were determined during the second heating cycle.

2.4. Fabrication of coatings

Powders of the urethane co-oligomer were dissolved in MEK at a concentration of about 8% (w/w) solids and used to prepare coatings by spraying the solutions onto a pre-cleaned Al substrate. The coatings were allowed to air dry in a low humidity chamber. The coatings were characterized by contact angle goniometry and subsequently subjected to fruit fly impact tests in both a benchtop wind tunnel and a larger-scale wind tunnel test facility.

2.5. Contact angle goniometry (CAG)

Water contact angle data were collected using a First Ten Angstroms FTA 1000B contact angle goniometer. Contact angle measurements of 8 μL water droplets were taken while tilting the axis from 0° to 60°. Prior to the experiment, interfacial tension measurements of the suspended water drops were taken to